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PATENT SPECIFICATION

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COMPLETE SPECIFICATION

NO DRAWINGS

Low Viscosity Polymer with Improved Pigment Dispersion

WE, IMPERIAL CHEMICAL INDUSTRIES LIMITED, of Imperial Chemical House, Millbank, London, S.W.1., a British Company, (Communicated by Canadian Industries Limited, a Canadian Corporation of 630 Dorchester Boulevard West, Montreal, Canada), do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:

This invention relates to a new process for obtaining synthetic linear polyesters of low intrinsic viscosity and which contain a pigment dispersed in a finely divided state, substantially free from aggregates or lumps of undispersed pigment. More particularly this process pertains to a method of obtaining finely divided carbon particles in a synthetic linear polyester of low intrinsic viscosity.

By "synthetic linear polyesters" are meant film-forming or fibre-forming condensation products of dicarboxylic acids such as terephthalic acid and glycols of the series $\text{HO}(\text{CH}_2)_n\text{OH}$ where n is an integer from 2 to 10. The most important example of this class of polyesters is polyethylene terephthalate which has enjoyed wide commercial success in both the film and fibre fields. Fabrics prepared from fibres of polyethylene terephthalate have become widely accepted and well known because of the ease with which they may be maintained. For example, such fabrics dry quickly after laundering, resist wrinkling and possess long-wearing qualities.

Fibres of polyethylene terephthalate destined for use in textile goods have in the past conveniently been provided in a black colour by incorporating finely divided carbon black in the polymer at an early stage of the polymerization process. This

black polymer may be melt spun in staple form and subsequently used to produce black cloth. Such black staple fibres may also be blended with white fibres to achieve a wide range of greys or alternatively, yarns made from such black fibre may be woven along with coloured yarns to achieve "effect" fabrics. The provision of such black polymer and the fibres melt spun therefrom provide a convenient and economic means of producing a black staple fibre or filament without the need of using conventional dyeing methods and processes on white or colourless fibres or the textiles made therefrom. In a similar fashion pigments of other colours may be incorporated in the polymer before melt spinning. However, because of the need to thoroughly clean processing equipment between batches of different colour, the incorporation of pigment into the polymer before melt spinning can normally only be economically justified in the production of fibres produced in large quantities, black fibres being such a product because of the wide use of black fibres in the textile trade.

The use of polyethylene terephthalate staple fibres for certain textile applications has in some cases been retarded by a characteristic known as "pilling," i.e. the formation of small balls on the surface of fabric due to the collection and entanglement of loose fibre ends. It has been proposed, for example, in British Patent Specification No. 840,796, that the tendency to "pill" in certain textile articles made from such staple fibres be reduced by reducing the molecular weight of the polymer by a fibre treatment process. It has more recently been proposed in British Specification No. 868,497 that "pilling" be reduced by spinning the staple fibres from polyethylene terephthalate polymers which

have a lower than normal viscosity. Such polymers are usually referred to as low Intrinsic Viscosity polymers or low I.V. polymers. It has been found, however, that while the fibres spun from such low Intrinsic Viscosity polymers possess the advantageous property of pilling resistance, the low I.V. polymers at the same time have a very poor carbon black dispersion rating, i.e. carbon black particles will not readily disperse uniformly throughout the polymers. The melt-spinning of a polymer with a poor carbon black particle dispersion is, as may be expected; very troublesome because of the large number of carbon lumps or aggregates present. The resultant yarn is of poor quality due to a large number of blebs or imperfections therein.

As is now well known from the disclosure of British Patent Specification No. 578079, linear, highly polymerized esters of terephthalic acid and glycols (e.g. polyethylene terephthalate) may be made by firstly, the esterification of terephthalic acid or an ester forming derivative of terephthalic acid with a glycol to form the appropriate glycol ester of terephthalic acid (ester interchange reaction) and, secondly, the formation from this ester of polymeric polyethylene terephthalate (polymerization reaction). To make a black polymer in such a process, it is necessary at some stage in the process to add carbon black to the polymer system. Because the dispersion of carbon black in glycol is normally of good quality, it is convenient to make up a relatively dilute slurry of carbon black in glycol and to add this to the ester interchange reaction vessel and in this way to utilize the glycol in the carbon black slurry as approximately 50% of the total glycol charge required for the batch. It has been noticed, however, that this initially good glycol/carbon black dispersion is destroyed during the ester interchange reaction and that aggregation of the carbon black particles occurs as ester interchange proceeds. However, during the polymerization reaction, the number of lumps or aggregates of carbon black again decreases as the viscosity of the polymer increases and as the shearing action within the polymerization reaction vessel increases. In this manner, the quality of the final carbon dispersion improves as polymerization continues to the standard polymer Intrinsic Viscosity. Until recently, every attempt to make a low I.V. black polymer, that is, a black polymer intended for an anti-pilling fibre, has resulted in a polymer of very poor carbon dispersion rating. This has been due in great part to lack of shearing action within the reaction vessel because of low polymer viscosity and a consequent diminution in the redispersion of aggregates of carbon black. Such low I.V. polymer

with poorly dispersed carbon black, as mentioned heretofore, is difficult to process in that agglomerates of carbon build up on the filter beds of spinneret packs resulting in short pack life and, additionally, the yarn produced therefrom may contain excessively large deposits of carbon black in some of its portions causing imperfections or blebs and points of weakness in the thread line.

It has now been discovered that the difficulties accompanying the dispersion of carbon black particles in a synthetic linear polyester, e.g. polyethylene terephthalate, of low Intrinsic Viscosity may be overcome without difficulty.

Accordingly, it is the object of the present invention to provide a process whereby particles of carbon black may be evenly and completely dispersed in a synthetic linear polyester having an Intrinsic Viscosity (as hereinafter defined) of 0.35 to 0.55, preferably of 0.40 to 0.50.

By 'Intrinsic Viscosity' is meant the reduced viscosity of the polymer at zero concentration, which may be determined by measuring the flow times of a polymer solution after successive dilutions with fresh solvent, calculating the reduced viscosities, and extrapolating a plot of the reduced viscosities against concentration to zero concentration. The reduced viscosity is obtained from the expression:—

$$\left(\frac{\text{Flow time of polymer solution} - 1}{\text{Flow time of solvent}} \right) \times \frac{1}{c}$$

wherein 'c' is the concentration expressed as grams of polymer per 100 ml. of solvent.

As used herein, the Intrinsic Viscosity was measured at 250°C. using orthochlorophenol as a solvent in a modified Ostwald viscometer.

The process of the present invention comprises the steps of producing a pigmented synthetic linear polyester e.g. polyethylene terephthalate, of normal Intrinsic Viscosity, that is, an Intrinsic Viscosity of about between 0.60 and 0.70, adding a depolymerizing agent such as a glycol, e.g. ethylene glycol, to the autoclave polymerization vessel under very slight vacuum to react nearly instantaneously with the polymer and depolymerize it to a substantially lower I.V. without an accompanying agglomeration of pigment particles, and then adjusting the polymerization conditions to produce a final product of desired low Intrinsic Viscosity.

In practical application, the process of the present invention allows the polymerization of a normal batch of black polymer of ethylene terephthalate to proceed until the Intrinsic Viscosity has reached a normal value of about 0.66. At this stage, any

carbon black aggregates have been well dispersed due to the high shear action of the agitator of the polymerization vessel moving in the viscous polymer. Ethylene glycol may then be added, in increments if desired, to the polymerization vessel where an almost instantaneous depolymerization of the polymer occurs. Such depolymerization occurs sufficiently quickly that no re-agglomeration of carbon black particles takes place. By the incremental addition of ethylene glycol to the polymer in the polymerization vessel, the degree of depolymerization of the polymer may be accurately measured by, for example, observation of the change in electrical power input to the agitator within the vessel. Where the Intrinsic Viscosity has been reduced below the desired level, that is, below about 0.45, the Intrinsic Viscosity may be increased again by the application of full vacuum to the polymerization vessel.

The following example illustrates but does not limit the invention.

25 **EXAMPLE**

100 parts of dimethyl terephthalate are mixed with 23.3 parts of ethylene glycol in a stainless steel kettle and heated to 150°C. to melt the D.M.T. To this was added, with stirring, a slurry composed of 2 parts of carbon black in 47.7 parts of ethylene glycol. This slurry had previously been recycled continuously through a sonic homogenizer for 6 hours and finally filtered through a 25 micron filter so that the slurry contained virtually no undispersed carbon particles. A suitable known esterifying catalyst in solution was added to the D.M.T.—glycol solution to speed up the reaction. Methanol was removed from the vessel as the temperature was gradually raised to 225°C., followed by the removal of excess glycol. The pressure was reduced gradually to 0.5 mm, while the temperature was raised to 278°C. The temperature and vacuum were maintained at these levels until the wattmeter measuring the power input to the stirrer of the vessel indicated a power increment corresponding to an I.V. of 0.66 if the polymer were then extruded. At this point the vacuum was released with dry nitrogen gas and by adjusting the nitrogen flow and the valve to the vacuum line a slight vacuum was maintained. 0.67 parts of ethylene glycol were added until the power increment was reduced to a level corresponding to an I.V. of 0.48. Full vacuum was applied again and in 10 minutes the power increment corresponded to an I.V. of 0.50. The polymer (polymer No. 1) was extruded.

A second batch of polymer (polymer No. 2), was prepared in the manner described above except that the polymer was not polymerized initially past an I.V. of 0.50

but was extruded directly.

Both of the polymers prepared as described had identical Intrinsic Viscosities. Microtome slices, 10 microns thick were made from polymer chips from each batch and compared at 400 x magnification with a set of standard photographs of polymer chips of varying quality with respect to carbon agglomerates. A rating of 1 refers to polymer containing a few agglomerates ranging from 5 to 10 microns per field of view while a rating of 4 refers to polymer containing a large number of agglomerates up to 40 microns in size per field of view. It was found that the low I.V. polymer prepared by the preferred process (polymer No. 1), was rated as better than 1 while the low I.V. polymer (polymer No. 2), prepared in the standard process had a rating of from 3-4.

Polymer No. 2 could not be spun satisfactorily through the type of filtering pack normally used for polymer containing well dispersed particles. By employing a coarse, less efficient pack filter, it was possible to obtain spun filaments from this polymer. The filaments obtained, however, contained a large number of surface imperfections caused by the presence of large aggregates of carbon. These faults in the spun yarn impaired the performance of this fibre in subsequent textile processing.

Polymer No. 1 on the other hand could be spun readily using the standard filtering pack. The spun yarn contained very few surface imperfections and performed well during the drawing stage and in textile processing.

It will be obvious to one skilled in the art that the depolymerization of normal I.V. black polymer as hereinbefore described need not be limited to the process whereby a glycol is added to the polymerization reaction vessel. For example, alternative depolymerization agents familiar in the art such as the monomer of ethylene terephthalate or steam may be employed to effect depolymerization. The use of ethylene glycol is, however, preferred. Similarly, the depolymerization step need not be confined to the autoclave reaction vessel but could, for example, be carried out at spinning by, for example, blending normal I.V. black chip with an appropriate depolymerizing agent. Depolymerization in the autoclave is, however, preferred because of the ease and accuracy by which the Intrinsic Viscosity of the polymer may be controlled. In addition, it will be equally obvious to one skilled in the art that the process of the present invention is not limited to the dispersion of carbon black in a low I.V. synthetic linear polyester but that other finely divided pigment additives may be used in the manner disclosed.

WHAT WE CLAIM IS:—

1. A process for the preparation of a synthetic linear polyester of low Intrinsic Viscosity of from 0.35 to 0.55, measured as
5 hereinbefore described having dispersed therein finely divided pigmenting material which is not soluble in the polyester comprising the steps of adding a pigmenting material to the reaction mixture prior to the
10 commencement of polycondensation, effecting polycondensation until the level of molecular weight of the resultant polyester attains that corresponding to an Intrinsic Viscosity of at least 0.6 with improved
15 dispersion therein of the pigmenting material, and then, by addition of a depolymerization agent rapidly reducing the molecular weight and viscosity of the pigmented linear polyester to a desired lower
20 molecular weight and viscosity without any significant change in the degree of dispersion in said polyester of said pigmenting material.
2. A process according to Claim 1 wherein the level of molecular weight of the polyester attains that corresponding to an
25 Intrinsic Viscosity at 0.6 to 0.7.
3. A process according to Claims 1 or 2 wherein the pigmenting material is carbon black.
4. A process according to Claims 1, 2 or
30 3 wherein the reduction of the molecular weight and viscosity of the linear polyester is accomplished by the addition of ethylene glycol to the polymer.
5. A process according to any of the
35 preceding claims wherein the polyester is poly (ethylene terephthalate).
6. A process for the preparation of synthetic linear polyester of low Intrinsic Viscosity substantially as hereinbefore
40 described.

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